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CHARACTERIZATION OF UNDOPED HIGH RESISTIVITY CdTe GROWN BY A THM METHOD

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Résumé. — Des mesures de temps de vol des porteurs dans des échantillons de tellurure de cadmium *purs* de haute résistivité ont montré la présence du niveau situé à $E_V + 0{,}15$ eV, généralement attribué à l'association impureté donatrice-lacune de cadmium. On a recherché, par différentes méthodes expérimentales, la nature de cette impureté.

Abstract. — Using time of flight technique, it is shown that the level at $E_V + 0.15$ eV, attributed generally to the association of a dopant impurity and a cadmium vacancy, is present in undoped materials. Several methods (TSC, SIMS, nuclear activation) have been used to investigate the nature of this impurity.

1. **Introduction.** — During the past years, the progress in the growth techniques of cadmium telluride crystals (CdTe) allowed to obtain high resistivity crystals of detector quality grade without intentionnal compensation with chemical dopants like indium or chlorine [1, 2]. The procedure used is as follows : in the first step, the vertical zone melting technique is used to purify the material. The obtained ingot is then used as source for the travelling heater method (THM) to grow the crystal. The crystallisation temperatures range from 700-900 °C at speeds of about 7 mm/day. These crystals have resistivities between 10^6-10^4 Ω.cm and detectors prepared with such material exhibit interesting properties : good energy resolution and absence of polarization.

Since it is generally believed that crystals of nearly stœchiometric composition cannot be grown without compensation, due to the particular shape of the phase diagram of CdTe, it seemed interesting to characterize these materials in order to determine wether or not they are compensated by chemical impurities. For this purpose, thermally stimulated current (TSC) measurements, time of flight studies, secondary ion mass spectroscopy (SIMS) and activation analyses have been performed.

2. **TSC measurements.** — In this method, a diode is made on the material under investigation. The device is cooled, while reverse biased, to low temperature and then illuminated with interband light, in order to fill the traps present in the crystal. When the temperature of the device is increased linearly as a function of time (at a rate β), the trapped carriers are reemitted at a temperature which depends on the activation energy of the center. This technique was successfully applied to compensated CdTe [3, 4]. The experimental results, obtained for two different undoped crystals are reported on figure 1. Three peaks are clearly resolved, located at 115, 140 and 195 K.

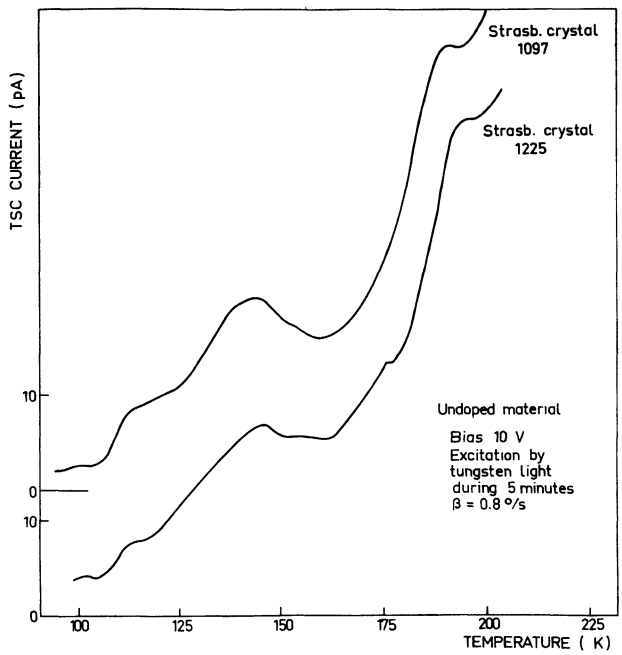

FIG. 1. — TSC spectra for two different undoped crystals.

For comparison, on figure 2, we have plotted the TSC curves obtained under identical conditions for chlorine compensated crystals of different origins. It is interesting to notice that these spectra have all the same structure, similar to that reported recently [3, 4]. The same peaks are present like in undoped materials,

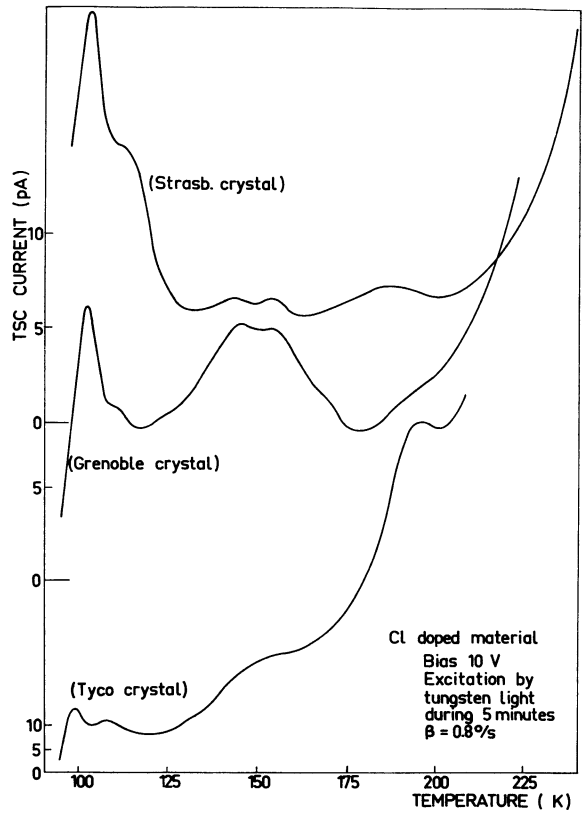

FIG. 2. — TSC curves for chlorine doped crystals

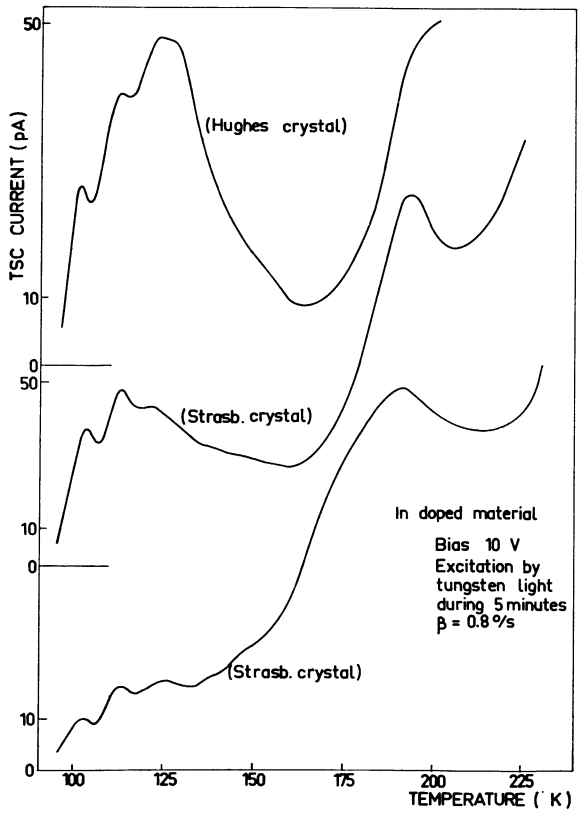

FIG. 3. — TSC spectra for indium doped crystals of various origin.

however, two additionnal peaks can be observed, located at 100 and 155 K. These results have also been compared to those obtained for indium compensated crystals of different origins. As shown on figure 3, the spectra have again the same structure for the various crystals. The *basic* peaks at 115, 140 and 155 K are present, the maximum at 100 K is present like in chlorine compensated crystals and a strong peak located at 125 K can be seen.

All the experimental results have been summarized in table I. The energies of the peaks have been esti-

TABLE I

Peak temperature (K)	Undoped	Cl doped	In doped	Estimated activation energy (eV)
—	—	—	—	—
100		X	X	0.19
110	X	X	X	$E_c - 0.23$
125			X	0.25
140	X	X		0.30
160		X		0.35
190	X	X	X	$E_v + 0.40$

mated by using either different classical methods [5] or by a special procedure [3, 6], which allowed us to identify the type of carrier which is trapped. The centers located at $E_c - 0.23$ eV, 0.30 eV and $E_v + 0.40$ eV are present in all crystals. The center with an activation energy of 0.19 eV is characteristic of the compensation either by chlorine or by indium. The 0.25 and 0.35 eV levels seem to be related respectively to the presence of indium and chlorine.

These results indicate clearly that undoped material contains less deep impurities than compensated crystals. Nevertheless, they do not allow to see if the material is compensated and the level at $E_v + 0.14$ eV cannot be observed in the temperature range used here. However, with the TSC technique it seems possible to determine the nature of the chemical element used for compensation.

3. **Time of flight technique.** — To investigate shallower levels, we used the time of flight method [7] and studied the transit across the detector of carriers generated by a pulsed electron gun. Figure 4 shows the evolution of electron and hole mobility as a function of temperature. The most interesting result is the strong decrease of the hole mobility at low temperature. Such a behaviour was also reported for compensated crystals and was attributed to a reduction of the hole mobility by multiple trapping and detrapping on a deep level. In our case, the same interpretation can be given since, as shown on figure 5, the mobility of the holes increases with the electric field at low temperature due to field assisted detrapping (Poole-Frenkel effect [8, 9]). An estimation of the concentration and activation energy of the trapping center responsible of the observed effect can be obtained by comparing the

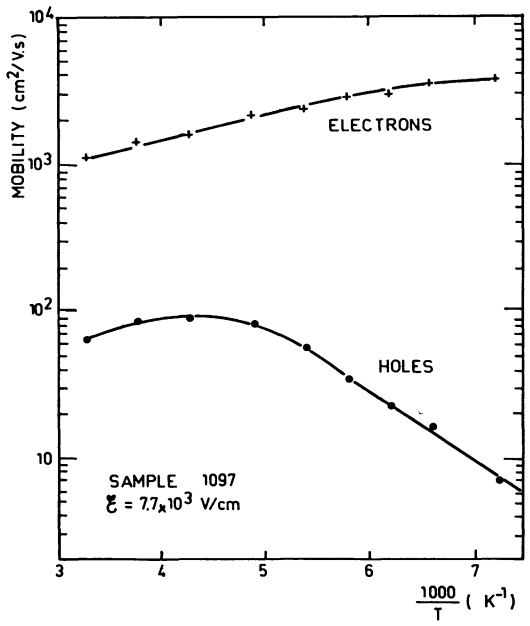

FIG. 4. — Electron and hole mobility in undoped crystals as a function of temperature.

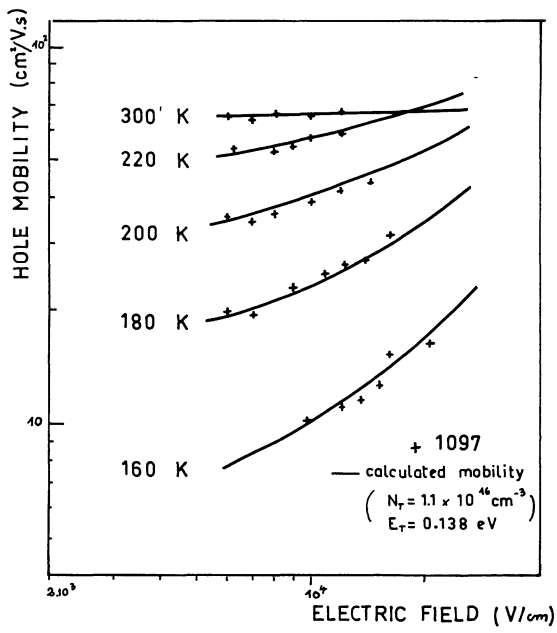

FIG. 5. — Variation of hole mobility with electrical field at various temperature.

experimental values of the mobility to that calculated, assuming that the mobility in the absence of trapping is given by the semi-empirical formula of Yamada [10] and using the tridimensional model of Hartke [11] for the Poole-Frenkel effect. A good agreement between experimental and theoretical results could be obtained for an activation energy of $E_T = 0.138$ eV and a trap concentration of 1.1×10^{16} cm^{-3}. The investigations performed on other undoped crystals lead to similar results.

According to the literature [9, 12] a level with the same activation energy (0.13-0.15 eV) has been found in crystals compensated with chlorine, bromine or indium, which is generally attributed to an association of one Cd vacancy with the donor used for the compensation. If this interpretation is correct, our results would clearly indicate that our nominally undoped material is in fact compensated by traces of group III or VII elements. Such a contamination may occur since undoped crystals are exposed to higher temperature than chlorine doped crystals during the zone refining process. Hence, it is not unlikely that the crystal is compensated by aluminium from the quartz tube as suggested in an earlier work [13], or by traces of fluorine coming from the etching of the quartz or even residual bromine due to the etching of the ingots.

However, a completely different hypothesis cannot be ruled out : the level at $E_v + 0.14$ eV may be related not to be the association between a cadmium vacancy and a group III or VII donor, but rather to an intrinsic defect, like interstitial tellurium. In this case the high resistivity of the crystals could only be explained by the presence in the material of a deep level fue to contamination by other chemical elements like carbon, for example. Therefore, chemical analysis are necessary to clarify this point.

4. **SIMS studies.** — An attempt was made to characterize undoped crystals by secondary ion mass spectrometry using a commercial instrument in which the ions scattered by a bombardment of 3 keV argon ions are analysed with a quadrupole spectrometer. This technique is basically a surface analysis method, but it may also give informations on the bulk if the crystal is bombarded for a long enough time.

The samples were prepared by polishing the surface with a diamond spray (grade 0.25 μ). The measurements were performed under vacuum with a residual pressure below 10^{-8} mm Hg. Since the material was of high resistivity, it was necessary to bombard the sample during the measurement with a beam of low energy electrons (3 keV) in order to avoid the built up of a positive space charge due to the primary ion beam.

Figures 6 and 7 show typical positive and negative ion spectra taken after removing a layer of 2 000 Å in thickness (at that depth the concentration of most elements was found to be constant). Besides Cd and Te (Cd does not appear as a negative ion) only a few ions are detected : Ar^{++}, Na^+, Mg^+, Al^+, Si^+, K^+, Ar^+ and C^-, O^-, F^-, CN^-, Cl^-. Surprisingly group III elements (aluminium) and group VII elements (chlorine, fluorine and sometimes bromine) are present. However, one should be careful before concluding that these impurities are responsible of the compensation and the presence of the level at $E_v + 0.15$ eV, since these contaminants like also sodium and magnesium are found is most SIMS experiments because of their high ionization cross section. It should be noted that the strong peak of argon is due to the ion beam.

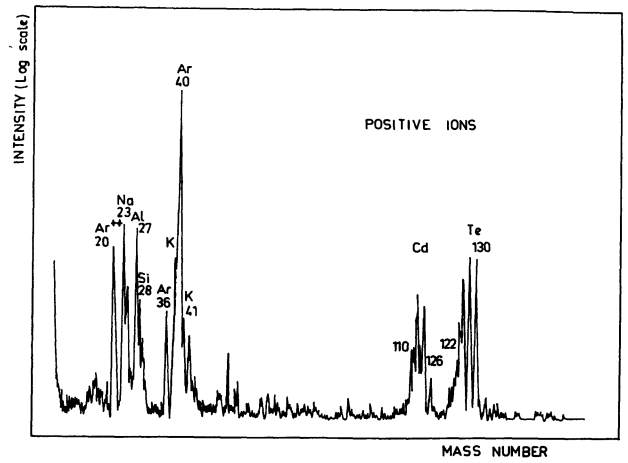

FIG. 6. — Positive ion SIMS spectrum in undoped crystals.

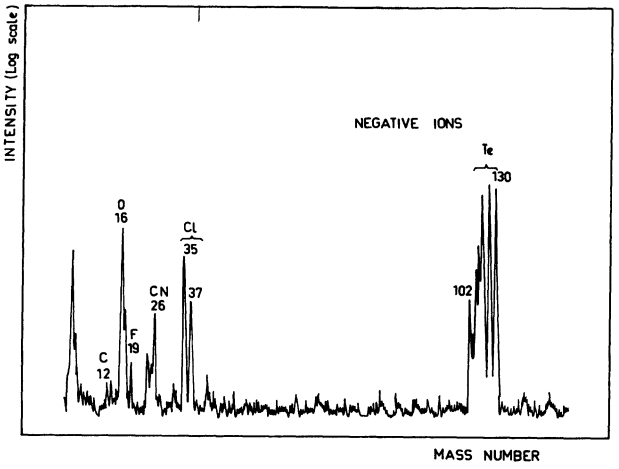

FIG. 7. — Negative ion SIMS spectrum in undoped crystals.

Finally, experiments performed on chlorine doped gave nearly identical spectra ; this may appear somewhat contradictory with the informations obtained by TSC but is probably due to the fact that SIMS is a less sensitive method than TSC.

5. **Activation analysis.** — To overcome this difficulty we have also performed nuclear activation analysis with tritons in the MeV range. Table II shows the

TABLE II

	Sample 1	2	3
S	0.4 ppm	1 ppm	0.5 ppm
Cl	2 ppm	2 ppm	—
Na	5 ppm	0.5 ppm	—
Mg	0.4 ppm	—	—
Mn	1 ppm	1 ppm	—
Al	75 ppb	4.3 ppm	0.2 ppm

detection limits of several elements in undoped samples. These data confirms the results of the SIMS measurements, since both chlorine and aluminium are present in most of the crystals. Furthermore, sodium and magnesium are found like in SIMS experiments.

6. **Conclusion.** — The level at $E_v + 0.15$ eV is present both in undoped and chlorine compensated crystals. This means that either our crystals are compensated by traces of group III or VII elements, or that the level at $E_v + 0.15$ eV is not related to the association vacancy-donor, but rather to an intrinsic defect, like tellurium. Chemical analysis indicate that halogens and aluminium are present in our crystals which, in principle, may be responsible of the compensation. However, the slope of the TSC curves in both kind of crystals is quite different, indicating a different chemical or impurity-defect structure. Therefore, further measurements are requested before a definite interpretation can be proposed.

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